ON THE ASSIGNMENTS OF THE VIBRATIONAL FREQUENCIES OF SOME BENZYL COMPOUNDS

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ABSTRACT. The Raman and infrared spectra of the molecules of benzyl chloride, benzyl bromide, benzyl cyanide and benzyl amine have been thoroughly investigated and a reasonably complete assignment of the vibrational frequencies in each case has been made.

INTRODUCTION

Assignments of the vibrational frequencies of benzene derivatives when the substituent is a single atom or a simple group of atoms have been made by numerous workers and as a result certain characteristic features of the vibrational spectra of such molecules are now easily recognised. However, when the substituent group is rather complicated the analysis of the vibrational spectrum of the whole molecule becomes difficult and reliable assignments of the vibrational frequencies have been made only in few cases. In a recent paper (Chattopadhyay *et al*, 1966) the assignment of the vibrational frequencies of benzyl acetate has been made and it has been pointed out that the assignment of the frequencies of vibration of the two constituent parts of the molecule could be made approximately independently. In the same paper it was also proposed to undertake the analysis of the vibrational spectra of other benzyl compounds.

The Raman spectra of a number of benzyl derivatives have been investigated by previous workers (Reitz *et al*, 1935; Sirkar *et al*, 1946; Ray, 1951 1952; Deb, 1961) and partial assignments of the vibrational freqeneeies of some of the molecules are given in Landolt and Börnstein Table (1951). The assignment of a number of infrared absorption bands of benzyl amine has been made by Leysen and Rysselberge (1963). In order to make assignments of the vibrational frequencies, the Raman and Infrared spectra of the benzyl chloride, bromide, cyanide and amine have been thoroughly investigated and assignments of the observed vibrational frequencies have been discussed in the present paper.

EXPERIMENTAL

Chemically pure samples of benzyl chloride, benzyl bromide, benzyl cyanide and benzyl amine obtained from B.D.H., Eastman Organic Chemicals and Ward Blenkinsop and Co. Ltd. were first fractionated and the proper fractions were

repeatedly distilled under reduced pressure before use. The Raman spectra of the compounds and the character of polarisation of the Raman lines were studied in the manner described in a previous paper (Chattopadhyay *et al*, 1966) with a Fuess glass spectrograph having dispersions of 13Å/mm and 19Å/mm in the Hg 4047Å and 4358Å regions respectively. The Raman spectrograms were obtained with different times of exposure and with appropriate filters in order to identify as many Raman lines as possible. The infrared spectra of the compounds in dilute solutions in different solvents and of the pure liquids were recorded on a Perkin Elmer Model 21 double beam infrared spectrophotometer with NaCl optics. The absorption spectra due to pure liquids were obtained with very thin films of the liquid formed between two NaCl discs and also in a cell of thickness .025mm, so that the existence of very weak absorption bands could be definitely ascertained.

RESULT

The frequency shifts of the Raman lines ($\Delta\nu$ in cm^{-1}) of benzyl chloride, bromide, cyanide and amine and the frequencies (ν in cm^{-1}) of the infrared absorption maxima of these compounds are given in Tables I-IV. The visually estimated intensities of the Raman lines are given in parentheses following the frequency-shift values and the states of polarisation are denoted by the letters P and D as usual. The Raman frequency-shifts reported by other workers together with the intensity values and nature of polarisation whenever available have been included in the appropriate Tables. The intensity and nature of the infrared absorption bands are denoted by the letters *s*-strong; *m*-medium; *w*-weak; *b*-broad; *sh*-shoulder and *v*-very. In the case of benzyl amine the table also includes the frequencies of the infrared absorption bands observed by Leysen and Rysselberge (1963).

The frequencies of vibration of all the molecules studied in the present investigation together with the proposed assignment are given in Table V. This Table also contains the assignments of some of the vibrational frequencies of these compounds according to Kohlrausch as given in Landolt Börnstein table (1951).

DISCUSSION

All the molecules of the benzyl compounds studied in this work, do not possess in the strictest sense any symmetry element other than the element of idenitity. However, under certain special configuration the molecules will have the symmetry of the point group C_s. In any case each of the molecules of benzyl chloride and benzyl bromide will have 39, benzyl cyanide 42 and benzyl amine 45 frequencies of vibration.

If the substituent group be treated as a single unit all the molecules will have approximately the symmetry of the point group C_{2v} and in that case there will

be thirty frequencies of vibration characteristic of the phenyl ring divided among the appropriate symmetry classes. On the other hand if the phenyl ring (denoted by ϕ) is treated as a single unit then the group ϕCH_2X will give rise to a characteristic vibrational modes whose number is 9 when X = Cl, or Br, 12 when X = CN and 15 if X represent the NH_2 group.

The assignments discussed in the following paragraphs have been made on the basis of the intensities in Raman scattering and infrared absorption, the character of polarisation of the Raman lines and the assignments made in the case of monohalobenzenes (Whiffen, 1956) and dihalomethanes (Herzberg, 1956; Landolt and Börnstein, 1951).

a) *Vibrational frequencies of the pnenyl ring* :

The frequencies of vibrations corresponding to the modes 6A, 6B (e_g^+); 8A, 8B(e_g^+); 9A. 9B(e_g^+); 18A(e_u^-) and 19A, 19B(e_u^-) of benzene are easily recognised in the vibrational spectra of the benzyl compounds and these are shown in Table V. The frequencies of the modes 10A (e_g^-), 16A(e_u^+) and 17A(e_u^+) in benzene are not expected to change much in monosubstituted benzenes and accordingly the weak Raman lines in the spectra of the benzyl compounds at about 405 cm^{-1} and 845 cm^{-1} have respectively been assigned to the modes 16A and 10A while the infrared bands in the region 940-970 cm^{-1} observed with the different benzyl compounds have been identified with the mode 17A.

All the benzyl compounds show very strong and well polarised Raman lines at about 1000 cm^{-1} and this frequency also appears as very weak absroption bands in the infrared spectra of these molecules. This band has been assigned to the mode $1a_{1g}$ of benzene.

The mode $12b_{1u}$ of benzene is mainly a in plane C-C-C angle deformation vibration with some stretching of the C = C bonds. Since the frequency of vibration of C-C-C angle deformation mode ($6Ae_g^+$) is considerably lowered on susbtitution, it is expected that the frequency of the mode $12b_{1u}$, would decrease when one of the H atom is replaced by a different atom or a group of atoms. Thus in fluoro- and chlorobenzene the strong polarised Raman lines at 806 cm^{-1} and 786 cm^{-1} have been assigned to this mode (Whiffen, 1956) while in toluene and ethyl benzene, which may be regarded as benzyl compounds, the frequencies corresponding to this mode are represented respectively by the well polarised Raman lines at 786 and 763cm^{-1}. In the spectra of the various benzyl derivatives there are strong polarised Raman lines in the frequency region 760-796 cm^{-1} and in the infrared spectra these frequencies appear as absorption bands of medium to strong intensity. These frequencies have been assigned to the mode $12b_{1u}$ of benzene.

In the Raman spectra of all the benzyl compounds there are well polarised and moderately strong lines in the frequency region 1200-1210 cm^{-1}. In infrared

absorption these frequencies in certain cases appear as strong bands. This frequency according to Whiffen (1956) is attributable to a trigonal mode involving considerable stretching of the C-X bond.

While this suggestion seems justified, it is difficult to determine the corresponding mode of vibration in benzene. However, it is evident that one of the C-H stretching vibrational modes of benzene is appropriately modified to give rise to this frequency in many monosubstituted benzenes. It is suggested that in this mode of vibration, the five CH groups in the phenyl ring move out as in mode 1 and for the remaining C-X group while the C atom moves out the atom Xmoves in, thereby compressing the C-X bond. Thus the frequency is due to a mode involving the stretching of the C -- C bonds and compression of the C-X bond.

The assignments of the remaining frequencies of the phenyl ring is made following Whiffen (1956). Thus the frequencies in the regions 1315-1330 cm^{-1} and 1376-1390 cm^{-1} which appear some times as weak Raman lines or weak infrared absorption bands in the spectra of the various benzyl compounds have respectively been assigned to the modes $3a_{2g}$ and $14b_{2u}$ of benzene. The mode $15b_{2u}$ of benzene is represented by the strong to moderately strong infrared bands in the region 1058-1072 cm^{-1} in the spectra of the molecules of the benzyl derivatives while the weak Raman line at about 990 cm^{-1} is assigned to the mode $5b_{2g}$.

In the case of monohalobenzenes Whiffen (1956) assigned the frequencies at about 680 and 740 cm^{-1} respectively to the modes $4b_{2g}$ and $11a_{2u}$ of benzene. However, from a consideration of the intensity in infrared absorption it appears justifiable that the very strong band at 695 cm^{-1} observed with all the compounds studied should correspond to the mode $11a_{2u}$ while the Raman band at about 750 cm^{-1} to the mode $4b_{2g}$.

Of the modes 10B(e_g^-), 16B (e_u^+), 17B(e_u^+) and 18B(e_u^-) of benzene the strong, depolarised Raman line of lowest frequency shift in the spectrum of the benzyl molecules is assigned to the mode 10B while the weak depolarised Raman line at 320 cm^{-1} may correspond to the mode 16B. The infrared active modes 17B and 18B have tentatively been identified with the infrared bands in the region 870-890 cm^{-1} and 910 -920 cm^{-1} respectively.

As with other monosubstituted benzenes, the benzyl derivatives will have five C-H stretching vibrational frequencies derived from any five of the modes $2a_{1g}$; 7A, 7B (e_g^+); $13b_{1u}$ and 20A, 20B(e_u^-) of benzene. One of these modes is converted into a C-X stretching mode of vibration while the other modes give rise to C-H stretching vibrational frequencies which are very nearly the same. Because of the inadequate dispersion of the spectrograph used and the limitations of the NaCl optics of infrared spectro-photometer it has not been possible to definitely ascertain all these vibrational frequencies. In the Raman spectra of all the

benzyl compounds there are broad polarised and moderately strong lines n the region 3050-3065 cm^{-1}. These frequencies in all probability arise from the mode 2 (a_{1g}) of benzene. The broadness of the lines may be due to the fact that Raman lines arising from the modes 7B and 13 of benzene have been superposed The very strong and broad infrared band at 3065 cm^{-1} in benzyl chloride and at 3100 cm^{-1} in benzyl amine may similarly arise in each case from the superposition of the bands due to the modes 20A and 20B of benzene.

Besides the above vibrational frequencies most of the benzyl compounds show weak to moderately strong and some times depolarised Raman lines in the frequency range 550-585 cm^{-1} and in many cases polarised and moderately strong lines at about 810 cm^{-1} which are absent in the spectra of monohalogenated benzenes. Also in benzyl chloride, ethyl benzene and benzyl mercaptan strong Raman lines are observed at 679, 672 and 673 cm^{-1} respectively corresponding to which no Raman lines are found in the spectra of the monohalobenzenes. These frequencies in all probability arise from the vibration of the ϕ CH_2X group of the molecules.

(b) *Vibrational frequencies of* ϕ CH_2X *group*

The most important vibrational frequencies of this group arise from the motion of the CH_2 group. This group gives rise to five distinct frequencies corresponding to one twisting mode, two rocking modes, one scissoring mode and two stretching modes of vibration. From a careful study of the assignments of the vibrational frequencies in dihalomethanes (Herzberg, 1956; Landolt and Börnstein, 1951) the frequencies of vibration which correspond to these modes in the benzyl compounds are easily identified. Thus the Raman lines in the various molecules appearing in the region 1400 cm-1440 cm^{-1} are attributed to the scissoring mode while one of the rocking modes gives rise to the Raman lines and infrared bands in the region 1220-1270 cm^{-1}. The other rocking mode of vibration in all probability is represented by the Raman lines of moderate intensity at about 810 cm^{-1} which also appear strongly in infrared absorption. The frequency of the CH_2-torsional motion in dihalomethanes is about 1150 cm^{-1} which changes only slightly if the mass of any of the halogen atoms is increased. This vibrational mode in the case of benzyl derivatives will have almost the same frequency as that of the modes 9B of the phenyl ring and thus has not been detected. The polarised Raman line of medium intensity at about 2970 cm^{-1} in the spectra of benzyl chloride and bromide and at about 2920 cm^{-1} in other benzyl compounds represents the symmetric CH stretching vibration of the CH_2 group. The asymmegric C-H stretching vibration in the dihalomethanes is about 3050 cm^{-1}. This frequency is not sensitive to the mass and nature of the halogen atoms and in the benzyl compounds would be expected to have almost the same frequency. But unfortunately this frequency is very close to the aromatic C-H stretching frequency in the phneyl ring and has

TABLE I

Benzyl chloride

Raman shifts ($\Delta\nu$ cm^{-1})		Infrared bands (ν cm^{-1})				
		Pure Liquids		Solution		
Landolt Börnstein (1951)	Present author	Thick film	Thin film	Carbon tetra chloride	Chloroform	Cyclo hexane
130(8sb)	137(5b)D					
269(3).61	267(3)P?					
330(2).89?	332(2)P					
470(5).28	472(4)P					
560(3).91	558(3)					
616(6).91	620(5)D					
679(10b)	673(6b)P		678 s			
700(3).25	700(1)?	695 vs	695 vs	695 vs	685 s	695 vs
766(6).61	764(4)P?		760 m			760 m
806(2)	813(3)D	810 vs	812 m		812 m	812 m
816(4).35						
	876(1)				890 sh	
		920 mb		930 vwb	930 sh	
		965 sh		952 sh	950 sh	955 vvw
		982 sh				985 vvw
1003(10).08	1000(10)P	1002 w		995 wb	1005 vvw	
1030(6).12	1030(4)P	1026 s	1028 w		1028 vvw	1025 vvwb
		1071 vs	1072 m	1065 wb	1072 m	1070 mb
1165(5)	1162(2)	1160 s	1155 vwb	1152 sh		
1182(2).74	1185(1)					
1209(7).20	1205(5)P	1210 mb	1210 wb	1210 mb	1210 sh	1208 m
1264(6).43	1258(5)D	1264 vs	1268 s	1265 vs	1268 vs	1262 vs
		1323 mb	1320 sh			
1382(0)		1390 wb				
1438(3)	1439(2)					
1452(1).97		1450 vs	1458 s	1458 m	1460 s	
	1497(2)	1498 s	1500 m	1500 m	1500 m	1495 s
1586(2)		1590 m				
1603(8).69	1607(5)D	1604 mb			1606 vvw	1606 vvwb
2964(1b)	2960(3)P	2983 sb	2990 mb			
	3024(1)	3030 sh		3020 sh		
3057(2b)	3057(6b)P		3058 mb	3050 wb		3052 mb
		3065 vsb				

TABLE II

Benzyl Bromide

Raman shifts ($\Delta\nu$ cm^{-1})			Infrared bands (ν cm^{-1})			
			Pure liquid		Solution in	
Reitz and Stockmair (1935)	Ray (1952)	Present author	Thick film	Thin film	Carbon tetra-chloride	carbon disul-phide
133 (10b)	103 (4)D	121 (6b)D				
236 (3)	239 (2)P	243 (4)P				
320 ($\frac{1}{2}$)		314 (1)				
452 (4)	448 (5b)P	459 (5)P				
548 (2)	544 (2)D	551 (5)D				
605 (10b)	601 (7b)P	613 (6b)D				
690 (0)			690 vs	688 vs	690 s	691 vs
755 (2)	749 (0)D	763 (3)D	751 s	750 vs	769 vsb	750 m
804 (2)	803 (1b)D	807 (3)D	800 wb	798 s	810 sh	805 vw
			888 sh	888 sh		
				910 vw	920 m	
				960 sh	970 wb	
1000 (6)	996 (5)P	1001 (10)P		1000 vw	1002 sh	
1027 (2)	1015 (0)P	1031 (4)P	1026 w	1026 w		1028 vvw
			1065 m	1065 s	1065 vwb	1061 vw
1114 (1)						
1163 (2b)	1162 (0)D	1165 (3)				
		1183 (2)				
		1205 (2)	1200 s	1200 vs	1202 m	
1222 (10b)	1221 (6b)P	1229 (6b)D	1224 s	1223 vs	1228 s	1222 s
		1315 (2)				
			1376 m			1380 sh
1438 (1)		1438 (2)	1440 sh	1444 wb	1440 sh	1421 sb
			1452 vs		1454 w	
1497 (1)		1494 (2)	1494 s	1494 vw		
		1537 (2)			1522 mb	
			1585 wb			1589 sh
1598 (6)	1595 (5b)D	1608 (6)D	1600 wb		1610 sh	1610 sh
	2949 (0)D					
	2970 (2)P	2969 (2)P				
	3054 (4b)P	3053 (4b)P	3040 sb	3052 sh	3053 mb	3048 mb

TABLE III

Benzyl cyanide

Raman shifts ($\Delta\nu$ cm^{-1})		Infrared bands (ν cm^{-1})				
		Pure Liquid		Solution in		
Landolt Börnstein (1951)	Present author	Thick film	Thin film	Carbon tetra chloride	Chloroform	Carbon disul-phide
126 (b)	135 (4)D					
216 (2sb)	216 (1)					
235 (3b)	236 (2)P					
322 (4)	323 (2)D					
358 (5)	360 (3)D					
428 (3b)	424 (3)P					
468 (1b)	470 (0)					
618 (7)	619 (5)D					
		696 vs	695 vs	692 vs	690 s	691 vs
		734 vs	734 vs			726 vs
744 (2)						
	751 (0)					
798 (6)	796 (4)P	780 vw	780 vvw			792 sh
812 (6b)	812 (4)P	805 vw				
849 (1)		882 vw	878 sh			
			925 mb			920 wb
					934 m	
		940 m				
		960 vvw				
991 (1)						
1003 (10)	1001 (10)P	1004 w	1004 vw	1002 sh		1000 sh
1031 (8)	1030 (4)P	1033 s	1030 m	1029 w	1028 w	1028 w
		1080 s	1076 mb		1080 w	1070 w
1157 (4)	1153 (3)P	1151 sh	1155 vw			1165 wb
1188 (4)	1189 (4)P	1190 w	1182 vw			
1192 (7)						
				1230 vwb?		
		1332 vvw	1331 vvw		1325 sh	
		1378 w	1388 sh			
1414 (5)	1413 (3)P	1421 vs	1420 sh	1418 m	1420 w	1414 s
		1458 s	1458 s	1454 m	1455 vs	
1499 (0)	1495 (2)D	1500 s	1500 s	1498 m	1499 s	
1586 (5)	1590 (1)	1590 sh	1586 sh		1584 s	
1602 (6)	1605 (4)D	1606 m	1604 m	1602 vvw	1604 m	1604 vvw
2252 (6)	2250 (4)P	2265 m	2262 sh	2268 w	2215 s	2260 w
2914 (5b)	2920 (4)P	2950 m	2924 w	2906 w		
2984 (3)						
3011 (3)						
3046 (3)						
3059 (9)		3050 m	3048 mb	3052 mb		3050 m
3065 (8b)	3069 (6b)P					

TABLE IV

Benzyl amine

Raman shift ($\Delta\nu$ cm^{-1})			Infrared bands (ν cm^{-1})	
Landolt Börnstein (1951)	Sirkar and Bishui (1946)	Present author	Pure Liquid Thin Film	Leyson and Rysselberge (1963)
168 (4b)	175 (2b)D	167 (4b)D		
404 (1)	412 (0b)	412 (2b)		
482 (2)	483 (0b)P	480 (2b)		
579 (1)		580 (1)		
620 (8)	628 (2)D	622 (5)D		
645 (0)				
			695 vs	696
	740 (0)		734 vsb	
750 (1)		751 (1)		
			770 (s)	
782 (5b)	786 (2)P	783 (4)P		
			810 s	797
846 (1)	834 (0)	846 (1)	836 vs sh	
			870 vsb	
			910 vs	
989 (1)			990 m	
1001 (10)	1007 (5)P	1002 (10)P	996 m	1000
1028 (6)	1030 (2)P	1024 (4)P	1024 m	1026
1058 (1)			1052 m	1058
1157 (5)	1160 (2)P	1156 (4)D	1150 vw	1153
1179 (2)		1175 (2)		
1202 (5)	1207 (4)P	1206 (4)P	1200 vw	
			1290 w	1290
			1320 w	
1390 (1)			1384 m	1383
	1402 (0)	1401 (1)		
1452 (2b)	1458 (3)D	1459 (2b)	1455 vs	1453
1491 (0)			1498 vs	1497
1582 (4)	1590 (1)D	1589 (2)	1598 vsb	
1604 (8)	1605 (8)D	1603 (5)D		1608
2859 (1)	2872 (2)P	2865 (2)	2865 s	
2946 (2)	2935 (3)P	2920 (2)	2925 s	
3006 (2)				
3035 (2)				
3054 (8)		3057 (5)P		
3062 (8)	3063 (10d)P		3100 vs	
3314 (2)	3316 (2)P	3312 (2)P		3289
3380 (0)				3378

TABLE V

Frequencies of vibration in Benzyl compounds

Present Author					Assignment due to Kohlrausch
Benzyl Chloride	Benzyl Bromide	Benzyl Cyanide	Benzyl Amine	Assignment and corresponding mode in Benzene	
137	121	135	157	10B e_g^-	
		216		CH_2X	
267	243	236		CH_2X	
332	314	323		16B e_u^+	
		360		CH_2X	
			412	16A e_u^+	
472	459	424	480	6A e_g^+	
		470		CH_2X	
558	551		580	CH_2X	
620	613	619	622	6B e_g^+	17 A & B e_u^+
673				CH_2X ?	
700 ?	690	696	695	11 a_2u	
	751	751	751	4 b_2g	5 b_{2g}
764	763	796	783	12 b_1u	
813	807	812	810	CH_2 Rock	
		849	846	10A e_g^-	10B & A e_g^-
876	888	882	870	17B e_u^+	
920	910	920	910	18B e_u^-	
965	970	940		17A e_u^+	
982		991	990	5 b_{2g}	
1000	1001	1001	1002	1 a_1g	
1030	1031	1030	1024	18A e_u^-	18A e_u^-
1071	1065	1076	1052	15 b_2u	
1162	1165	1153	1156	9B e_g^+ + CH_2 twist	9B e_g^+
1185	1183	1189	1175	9A e_g^+	9A e_g^+
1205	1205	1192	1206	ν (CH_2–X)	
1258	1229	1230		CH_2-Rock	

TABLE V (*contd.*)

Present Autohr					
Benzyl Chloride	Benzyl Bromide	Benzyl Cyanide	Benzyl Amine	Assignment and corresponding mode in Benzene	Assignment due to Kohlrausch
			1290	?	
1323	1315	1331	1320	3 a_{2g}	3 a_{2g}
1390	1376	1378	1384	14 b_{2u}	15 b_{2u}
1439	1438	1418	1401	CH_2-Scissor	
1450	1452	1455	1449	19B e_u^-	
1497	1494	1495	1498	19A e_u^-	
1590	1585	1590	1589	8A e_g^+	
1607	1608	1605	1603	8B e_g^+	
		2250		ν (C ≡ N)	
			2865	?	
2960	2969	2920	2920	ν $(CH)_s$ of CH_2X	
3024		3046	3035		
		3059			
3057	3053	3069	3057	2 a_{1g}	
				7B e_g^+	
			3062	13 b_{1u}	
3065			3100	20A e_u^-	
				20B e_u^-	
			3312	ν $(NH)_s$	
			3378	ν $(NH)_a$	

not been identified. In the Raman spectra of benzyl chloride, benzyl bromide and benzyl cyanide there are polarised Raman lines of medium intensity at 267, 243 and 236 cm^{-1} respectively. These frequencies might arise from a mode of vibration similar to that giving rise to a strong polarised Raman line at 283 cm^{-1} in dichloromethane (Herzberg, 1956). All the proposed assignments are given in table V.

Besides the frequencies arising out of the vibrations of CH_2 group there are certain characteristic group frequencies which are easily recognised. The strong polarised Raman line at 2250 cm^{-1} in benzyl cyanide arises from the stretching vibration of the C≡N bond. The intensity and position of the nitrile band in the infrared absorption spectra due to solutions in different solvents are found to alter considerably.

In the case of benzyl amine a weak polarised Raman line at 3312 cm^{-1} has been observed. Reitz and Stockmair (1935) have reported two bands at 3307 and 3385 cm^{-1} of which the latter is very weak. Leysen and Rysselberge (1963) have observed two bands at 3289 and 3378 cm^{-1} in the infrared spectrum of benzyl amine. These two bands are easily assigned respectively to the symmetric and asymmetric N-H stretching vibrational frequencies of the NH_2 group. In addition to the frequencies of vibration whose assignments have been discussed above there are certain other frequencies in the spectra of the benzyl compounds which in all probability arise from the vibration of the ϕ CH_2X group. These frequencies are marked in table V but no attempt has been made to propose any definite assignment of these frequencies.

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